Chapter 10 Assessing Air Quality: Monitoring

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10.1 Introduction

In environmental investigations, the term "monitoring" describes the collection of actual samples of environmental media and then subjecting those samples (usually) to chemical analysis to determine the identity and concentration of the various pollutants in the sample. A distinction may also be made between sampling (i.e., stack testing) and monitoring (i.e., for ambient concentrations). In air toxics risk assessment, this process commonly consists of collecting air samples and either evaluating the samples at the monitoring station itself, or sending them to a laboratory for evaluation.

For air toxics risk assessments, monitoring and analysis can help determine the concentration of both those pollutants in air and those that have migrated into other media, such as soil, water, sediments, and biota. This chapter discusses the use of monitoring to evaluate pollutants in air. Chapter 19 discusses the use of monitoring in media other than air.

Many aspects of a monitoring program will depend on the spatial scale of the assessment being supported by the measurement program:

- **Micro-scale** – highly localized regions up to 100 meters in size; these might reflect city blocks or individual households.

- **Middle-scale** – regions of several blocks with sizes of 100 to 500 meters.

- **Neighborhood-scale** – an extended area with uniform land use (and, hence, relatively homogeneous receptor population), extending up to several kilometers in size.

- **Urban-scale** – overall city or county conditions, perhaps up to 50 km in size.

- **Regional- or national-scale** – a state, several states, or the entire nation.

Air toxics risk assessments often examine exposure to relatively large numbers of people over relatively large geographic areas (e.g., a neighborhood or urban area, county, or larger). In these instances, the risk managers and analysts must carefully use their planning and scoping activities to develop the questions they want to answer and identifying the types of data they will need to answer those questions. For some questions and data needs, monitoring is the preferred tool for estimating inhalation exposure concentrations for air toxics risk assessment, either as the primary way of determining concentrations in air or as a way to test and normalize model results (and look for gaps in the emissions inventory).

This chapter provides an overview of monitoring, including recent advances by EPA (Section 10.2); the reasons for monitoring (Section 10.3); how to plan a monitoring program (Section 10.4); implementation (Section 10.5); available air monitoring methods (Section 10.6); archiving monitoring data (Section 10.7); and using monitoring data to evaluate source contribution (Section 10.8).

10.2 Air Toxics Monitoring: Recent Advances

EPA recently published a draft *National Air Toxics Monitoring Strategy* that describes the structure of the national air toxics monitoring program, including its history, status, and expected products.[1] At the start of the program, EPA's focus was on "nationally pervasive" priority pollutants. In recent years, EPA has initiated local scale monitoring studies to address potential air toxics problem areas.

EPA's Ambient Monitoring Technology Information Center (AMTIC)

AMTIC (http://www.epa.gov/ttn/amtic/welcome.html) is centered around the exchange of ambient monitoring related information. Established in 1991 as an electronic Bulletin Board System (BBS), AMTIC has evolved with changing technology into a page on the World Wide Web. AMTIC is operated by EPA's Office of Air Quality Planning and Standards (OAQPS) through the Monitoring and Quality Assurance Group (MQAG). AMTIC contains information on all the Reference and Equivalent methods for the Criteria pollutants, the toxic organics (TO) Methods for air toxics and other noncriteria pollutant methodologies, Federal Regulations pertaining to ambient monitoring, ambient monitoring quality assurance/quality control (QA/QC) related information, information on ambient monitoring related publications, ambient monitoring news, field and laboratory studies of interest, and updates on any new or developing EPA Ambient Air standards.

EPA's air toxics monitoring is structured into four groups – national level, local scale, persistent bioaccumulative toxics (PBTs), and "other" EPA-specific programs.

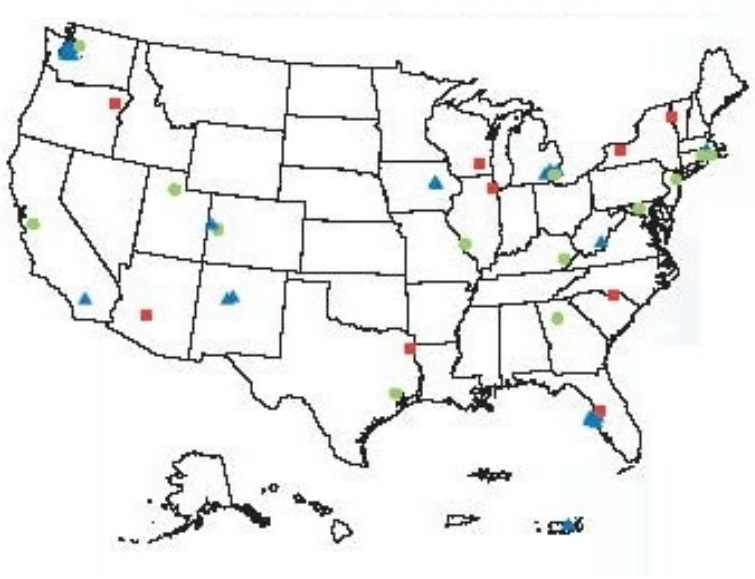
- The National Air Toxics Trends System (NATTS) program is a network of monitoring stations at 22 urban or rural locations across the country (see Exhibit 10-1). The focus for these sites is on seven "nationally pervasive" priority pollutants (formaldehyde, arsenic, chromium, benzene, 1,3-butadiene, acrolein, and light absorbing carbon). All of the stations are expected to become operational in early 2004.

- Local scale monitoring studies are designed to complement NATTS, but they are shorter-term (less than 2 years) and have more flexible study requirements to go beyond the scope of the NATTS. Local-level studies provide information of urban/local interest that is not achievable with a single monitoring site at a city. For example, these studies may address specific source categories or better characterize pollutant levels associated with different locations in a metropolitan area. EPA plans to implement 10 to 15 local scale monitoring projects that are implemented by state, local, and tribal (S/L/T) air pollution control agencies.

- Programs that monitor atmospheric deposition of PBTs include (1) the National Atmospheric Deposition Program – Mercury Deposition Network (NADP – MDN), a multi-agency program with approximately 90 monitoring sites; (2) the Integrated Atmospheric Deposition Network (IADN), a partnership between EPA and Canada, which is measuring PBTs in the Great Lakes Region; and (3) the National Dioxin Air Monitoring Network (NDAMN), a 30-site research program.

- A variety of EPA Regional air toxics monitoring activities that existed prior to NATTS continue.

Exhibit 10-1. National Air Toxics Trends Stations (NATTS) Sites



January 2003 Startup	January 2004 Startup	Pilot Programs
Providence, RI	Chittenden County, VT*	Barcelona/San Juan, PR
Roxbury, MA	Rochester, NY	Providence, RI
New York, NY	Tampa, FL	Keeney Knob, WV*
Washington, DC	Chesterfield, SC*	Tampa, FL
Decatur (Atlanta), GA	Chicago, IL	Detroit, MI
Hazard, KY*	Mayville, WI	Rio Rancho, NM
Detroit, MI	Harrison County, TX*	Cedar Rapids, IA
Deer Park (Houston), TX	Phoenix, AZ	San Jacinto, CA
St. Louis, MO	La Grande, OR*	Grand Junction, CO*
Bountiful, UT		Seattle, WA
Grand Junction, CO*		
San Jose, CA		
Seattle, WA		* rural site

Source: EPA's *Latest Findings on National Air Quality*[2]

EPA has encouraged a significant effort over the past few years to increase reporting of air toxics sampling results to EPA's AirData database website (http://www.epa.gov/air/data). For example, the Lake Michigan Air Directors Consortium (LADCO), the Northeast States for Coordinated Air Use Management (NESCAUM), and the California Air Resources Board (CARB) "mined" existing data from approximately 300 existing monitoring sites across the U.S. to provide information about the spatial pattern, temporal profile, and general characteristics of air toxics compounds. EPA collected additional data for this analysis from a year long monitoring study carried out in four urban areas and six smaller city/rural areas. A number of reports, newsletters, and related documents describing EPA's air toxics monitoring efforts are available at EPA's Ambient Monitoring Technology Information Center website.[3]

10.3 Monitoring for Air Toxics Risk Assessments: Why Monitor?

Air toxics programs have long used monitoring to evaluate the concentration of chemicals in air. In general, monitoring (sampling and analysis) results may help:

- Identify and estimate current exposures to ambient concentrations of air toxics (outdoor and/or indoor) at a specific location of concern (e.g., a school or neighborhood). As an example, EPA tracks ozone concentrations at numerous locations around the country, with results available over the Internet (http://www.epa.gov/airnow/) for many locations, virtually in real-time. As another example, air toxics monitoring can be used to evaluate the impacts of a specific source on a nearby receptor ("source-oriented" monitoring).

- Develop or refine values for specific parameters needed by air dispersion models (for example, study-specific release data, meteorological conditions).

- Validate the predictions of a model in specified circumstances (e.g. validate that the location of highest exposure predicted by the model is correct, which increases confidence that a maximally exposed subpopulation has been identified – may be difficult to do without a very dense monitoring network).

- Track trends in air quality levels (e.g. to determine whether air pollution programs have generally been effective at reducing exposures).

- Identify gaps in emissions inventories (e.g., monitoring identifies an airborne chemical that is not reported in existing emissions inventories) or close gaps that might be present in existing data (e.g., concentrations of specific air toxics in specific releases).

- Determine compliance with air toxics legal requirements (e.g., permit limits at a factory, emissions limitations on motor vehicles).

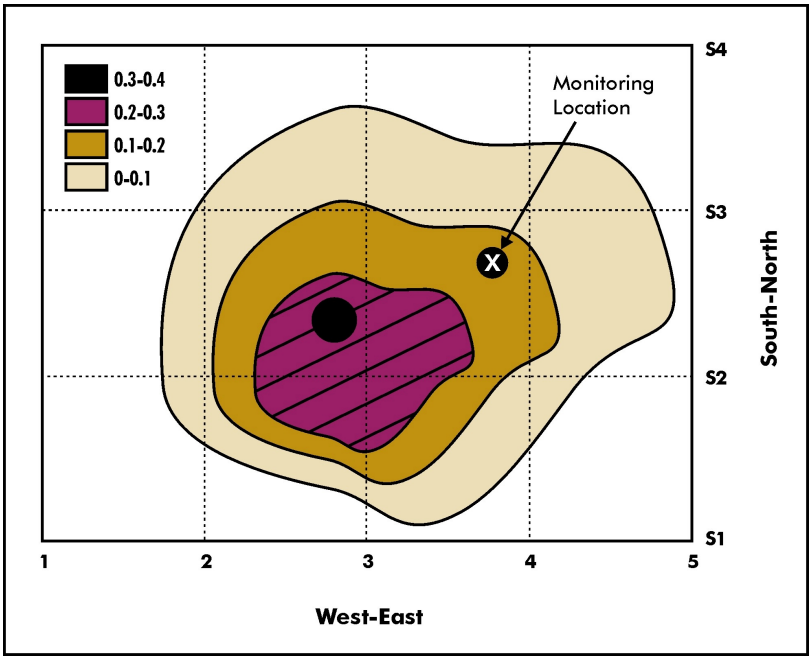
- Gather data in support of enforcement actions.

Ultimately, the choice of whether to monitor or model (or both) depends on the goals of the assessment, the exposure setting, other specific project circumstances (e.g., many communities want monitoring as part of a risk assessment), and the assessing entity. For example, to understand the exposure an actual individual receives as they move about their daily activities, personal monitoring is the best option because it reflects the pattern of this movement. However, such studies are rarely done outside of research settings. As another example, compliance with a permitted release rate may also require monitoring as the preferred method of measurement. Exhibit 10-2 provides a brief comparison of modeling versus monitoring.

Exhibit 10-2. Comparison of Modeling and Monitoring Approaches for Estimating Ambient Air Exposure Concentrations (ECs)	
Modeling	**Monitoring**
Modeling is relatively fast and inexpensive compared to monitoring. Many screening-level models can be run in spreadsheet formats and require relatively simple input parameters. Many dispersion models, along with technical reference manuals and other support documents, are available for free download from EPA's Support Center for Regulatory Air Models (SCRAM) website (http://www.epa.gov/ttn/scram/). Resources normally need to be expended to enhance the local air toxics emission inventories to make air toxics modeling more precise.	With monitoring, it takes time to build data, and there are methodological limits and logistical issues. How expensive monitoring is depends on what you are trying to do and how much you are willing to pay. Monitoring does not always require equipment purchase, and some states and local areas already have equipment. Some less expensive monitoring techniques are now available (e.g., passive samplers).
Modeling results can estimate concentrations over a large spatial area (e.g., a 50-km radius from a source) and can provide a "big picture" view of the assessment area. Modeling also allows for analysis of EC at multiple points throughout the assessment area. The downside of modeling, however, is that these are predicted concentrations.	Monitoring results provide actual measured concentrations. Multiple locations may be required to characterize concentrations over an area, although Geographic Information Systems (GIS) methods facilitate interpolation between locations. The downside is that the monitoring may not be representative of a large geographic area.
Screening-level models can provide a predicted estimate of whether significant concentrations are likely. A simple screening analysis may be sufficient to make a risk management decision that no action is required.	Monitoring can be used to identify and measure exposures for specific individuals at a specific location of concern (e.g., a school). This data can provide a quick screen to determine whether more extensive monitoring is needed.
Models can be used to identify areas where maximum concentrations are likely to occur, and thus where to focus efforts for additional tiers of the assessment. Uncertainties in model parameters and the discrete division of the wind field used in models (often with only eight wind directions) can result in incorrect identification of the locations of maximum concentration.	Monitoring can identify areas and actual levels of exposure occurring at the monitoring sites. Monitoring can also be used to indicate the point of maximal exposure if the monitoring is designed for that purpose. The selection of the monitoring locations is critical; if placed in the wrong locations, monitors can provide incorrect and misleading information about maximal exposures.
Models can be used to identify the subset of chemicals of potential concern (COPCs) and exposure pathways/routes that have the greatest contribution to risk. This can be helpful in focusing efforts for additional tiers of the assessment as well as determining appropriate risk management actions.	Monitoring can be used to confirm significant exposure pathways and routes. (Measured concentrations can be compared to risk-based screening levels). It also can be used to identify compounds that may not have been suspected and, hence, were not included in models (i.e., monitoring allows identification of gaps in the emissions inventory).
Models allow "what if" scenarios to be evaluated (e.g., what if a permitted emission were doubled?).	Monitoring can only evaluate current conditions.
More complex modeling may allow explicit predictions and estimates of variability in exposure.	A large number of samples generally is needed to characterize variability; this may be prohibitively expensive. Monitoring, however, provides a direct and reliable means to characterize variability.
Models often use simplifying assumptions and data inputs that may or may not be representative of the specific assessment area. This introduces uncertainty into model predictions.	Monitoring can be used to confirm actual exposure levels, to investigate assumptions or calibrate models to site-specific conditions, and to close gaps in data, reducing uncertainties.

Air toxics risk assessments, however, tend to examine potential exposures to hazardous air pollutants (HAPs) and other air toxics for a relatively large number of people over relatively large geographic areas (e.g., a neighborhood or urban area, county, or larger). In these instances, the risk managers and analysts must carefully use their planning and scoping activities to develop the questions they want to answer and to identify the types of data they will need to answer those questions. For some questions and data needs, monitoring is the preferred tool. For others, modeling is better. In general, most air toxics risk assessments will benefit from some combination of both modeling and monitoring to provide the depth and breadth of information that will be necessary to answer the assessment questions (see hypothetical example in Exhibit 10-3).

Exhibit 10-3. Hypothetical Example of a Combined Modeling and Monitoring Program



This figure illustrates a hypothetical set of isopleths for annual average air concentrations that a dispersion model predicted, assuming a single source (black dot) near the center of the geographic region. Note that the model predicts the point of maximal exposure to be somewhere within the area bounded by grid points 2, 4, S1, and S3, based on the existing information on release rate, wind direction, and effective release height. In this hypothetical example, a monitoring station was used to measure ambient concentrations as a means of evaluating the model predictions. Note that the monitoring location is not in the area of estimated highest concentration and, therefore, might not provide a better estimate of maximum exposure.

Indeed, most air toxics risk assessments that evaluate exposures to populations receiving impacts from one or more sources should generally consider using modeling as their primary tool to evaluate and characterize exposures and risks. In certain instances, assessors may use monitoring as the primary tool to evaluate exposure concentrations for potentially exposed populations. The utility of modeling for neighborhood and larger scale analyses is that it provides a better picture of the variation of exposure conditions over the assessment area domain (i.e., modeling provides spatial resolution) and allows a more straightforward approach to source allocation (i.e., what portion of the risk is caused by each of the modeled sources).

Monitoring, on the other hand, only provides estimates of concentrations at the point at which samples are taken, and it is often difficult to clearly define the spatial coverage that those measured concentrations represent. In addition, it is often difficult to use monitoring data for source allocation (especially for chemicals emitted by numerous sources). Monitoring plays a crucial role in identifying important chemicals that the emissions inventories may not have captured. In rarer instances, assessors can use monitoring as the primary tool to evaluate exposures for potentially exposed populations; however, this method carries a corresponding increase in the uncertainty of the results (see Section 10.4 on how to use ambient monitoring data to develop estimates of exposure concentration). (Note that, in limited circumstances, geostatistical techniques such as kriging are sometimes applied to estimate concentration variation between a set of monitors. This topic is beyond the scope of this reference manual; however, assessors are encouraged to carefully consider the uncertainties associated with this type of approach and whether alternate tools, such as air dispersion modeling, would provide a better understanding of concentration gradients across the study area. In addition, the average concentration of atmospheric pollutants across a study area is sometimes estimated by averaging the results of all the monitors in the area. However, since pollutant concentration can change rapidly across space and time, combining data across monitors may "average out" very important information about exposure at a particular monitoring location. It is for this reason that combining data across monitors is not commonly performed and assessors are encourage to carefully consider the pros and cons of attempting such an analysis. If monitors are combined, the results should, nevertheless, be reported alongside the results of each of the individual monitors.)

If assessors make the choice to implement a monitoring program, it is important to carefully design the sampling and analysis approach to provide meaningful input into the risk management decision. Because sampling and analysis are relatively expensive and time consuming, a well-designed monitoring program can ensure the efficient use of resources. Well designed and implemented monitoring programs quantify not only the concentrations but also information related to the associated data uncertainty. The study-specific conceptual model and analysis plan that assessors develop during the planning and scoping phase help ensure a well-designed sampling and analysis program that will yield results suitable for decision-making purposes. Monitoring programs are commonly designed to:

- Use a sampling methodology that results in scientifically defensible data and that meets regulatory criteria or other concerns – it is important to utilize methodologies that are scientifically defensible and acceptable within a regulatory context;

- Identify and quantify air toxics (or their breakdown products) of interest with respect to contribution to risk in all media of interest (including, in some cases, non-air media; see Chapter 19);

- Attain quantitation requirements (e.g., quantitation limits) sufficient to compare to dose-response values (e.g., the sensitivity should be sufficient to allow reliable measurements below concentrations anticipated to produce adverse health effects);

- Demonstrate acceptable confidence in the data set to be used for decision-making based on quality assurance benchmarks including benchmarks for precision, accuracy, representativeness, completeness, and comparability; and

- Provide for a clear and unambiguous data validation and reporting methodology so monitoring results can be tracked, verified, and validated when they are used in decisions.

The design of a monitoring program that meets data quality objectives (DQO) and quality assurance project plan (QAPP) requirements depends on the answers to four questions:

1. **What is the risk management decision to be made, and how will assessors use monitoring results in that decision?** Monitoring programs typically are a component of risk assessments that support risk management decisions; these decisions normally focus on how best to reduce risks from exposure to air toxics through reducing or otherwise limiting emissions.

Quality Assurance Project Plan (QAPP) and Data Quality Objectives (DQO) Process

As Chapter 6 introduced, a QAPP is part of the overall risk assessment analysis plan that ensures the quality of data used in decisions. Generally included in the data quality program is the DQO process, which establishes the criteria that must be met if data are to meet the needs of a decision-maker (e.g. it establishes the error bounds on data, which are related in turn to the uncertainties a decision-maker, can tolerate in reaching a defensible decision). Assessors can accomplish this goal through the following seven steps:[(a)]

1. State the problem.
2. Identify the decision to be made.
3. Identify inputs to the decision (i.e., which data are needed).
4. Define the study boundaries (i.e., what factors, scenarios, etc., will be included in the study to produce these data).
5. Develop a decision rule (i.e., how the data will relate to a specific decision to be made).
6. Specify limits on decision errors (i.e., how much uncertainty can exist and still allow a defensible decision to be made).
7. Optimize the design of the study to ensure the data quality meets the decision rule.

The QAPP specifies precisely how to collect and analyze the data to meet the goals established by the DQO process. The QAPP establishes specific procedures that assessors follow to meet DQOs. These DQOs include procedures for identifying reliable methods, choosing sample locations and frequencies, handling samples, calibration of equipment, recording and archiving of data, and analysis of the data. The DQO goal is to ensure that all members of the project team understand, and follow, procedures that will ensure the results of the study meet the data quality needs of a decision. Once these DQOs have been established, it is necessary to develop a plan as to how the participants will meet them in practice while collecting the data for the study.

[(a)]U.S. Environmental Protection Agency (EPA). 1994. *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, Office of Research and Development, EPA/600/R-96/055; available at http://ww.epa.gov/swerust1/cat/epaqag4.pdf.

2. **How accurately must the results be to be useful in these decisions?** The reliability of monitoring program results must be adequate for the needs of the risk management decision. For example, risk assessors need to quantify air concentrations and/or exposures within some bounds of accuracy and/or precision. It is important to meet these criteria of accuracy and precision, but not necessarily to exceed them. As noted in Appendix H, the data quality objectives must provide results that allow reliable decision-making. However, resources that participants devote to one aspect of a monitoring program, such as choosing a larger number of sampling sites, will draw resources away from another aspect of the program, such as sampling for a larger number of air toxics. This is why it is essential to understand fully the decision that the given set of results will support, other results that assessors will need to support that same decision, and how participants can balance monitoring results across these different data needs to reduce the levels of uncertainty to acceptable levels. Assessors can achieve this goal by conducting a **sensitivity analysis**[a], which determines what aspects of a full monitoring program will require the greatest attention and resources; monitoring results that play the most significant role in a decision may require the greatest allocation of resources.

3. **What methodologies are available to monitor at a particular level of quality?** The choice of monitoring method depends on the specific air toxic(s) to be analyzed, the objective of the monitoring (as the DQOs specified), the time over which a result is to apply, and available resources. It is important to note here that there do not currently exist valid methods (either field, lab, or both) for a large number of chemicals that may be of interest; for methods that do exist, the achievable sensitivity may not match the DQOs (this is another reason that modeling is often used as the primary decision making tool since these issues are irrelevant to models).

4. **What resources are available for the monitoring program?** The choice of a monitoring strategy often depends primarily on available resources (e.g., time, money). These factors are of particular concern in air toxics monitoring because most studies of chronic exposure generally require a minimum of one full year of data to characterize chronic exposure. It is not uncommon to have a lag time of two years or more from the beginning of a monitoring study to a final report when one considers the time it takes to plan the monitoring study, obtain access to land, build the monitoring structures, run the study, analyze the samples, validate the results, and write the data report.

10.4 Planning for Air Toxics Monitoring

As noted above, planning is a critical part of any air toxics monitoring program. The discussion of planning below first describes a recommended general approach (Section 10.4.1) and then outlines several specific planning issues (Section 10.4.2). EPA has developed resources that provide additional details on operating procedures, with discussions of data quality issues, definitions, and applications to specific methodologies.[4]

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[a] A sensitivity analysis shows the relative effect of uncertainty in each aspect of an assessment on the overall uncertainty in that assessment. Ideally the data quality objectives will be more stringent for those measurements that play a larger role in the final decision, since narrowing the uncertainty in these measurements significantly reduces uncertainty associated with the decision.

10.4.1 General Planning Approach

Planning an air toxics monitoring program involves a step-wise integration of sampling protocols with data quality criteria and data analysis processes that are consistent with the study-specific conceptual model (CM), QAPP, and DQO processes. Although presented step-wise, the process is actually iterative, and decisions at one step may require verification or modification of assumptions or decisions made at previous steps.

1. **Understand the problem**. As noted above, assessors may design monitoring programs to support a number of different types of management decisions. For risk assessments, the CM can focus participants' understanding of both the scope and the breadth of the problem that the sampling and analysis are to address. The ***most important questions to answer*** immediately are: whether assessors will use monitoring results to characterize exposure and risk, whether they will use results to evaluate air quality model performance and look for gaps in the emissions inventory, or whether they will use results for both reasons. This is a ***critical question for participants to answer***, because the data needs can be drastically different, depending on how the assessors will use the monitoring data.

2. **Identify existing data**. Sampling and analysis for risk assessment may not be necessary if the information to be developed is already available from other sources and meets the quality requirements for decision making. The data sources discussed in Chapter 4 may provide sufficient information for the risk management decision.

Examples of Study-Specific Questions

- What is the maximum plausible value of EC for the population in a geographic region, taking into account spatial and temporal variability and uncertainty?
- What is the location of this maximal value within the geographic region?
- Which air toxics are found at the highest concentrations with respect to their dose-response values (e.g., which air toxics have the greatest potential to produce a hazard quotient above one)?
- Do monitoring results generally agree or disagree with the value of air concentrations identified by existing models?

3. **Itemize data needs**. Where existing data are insufficient to answer the study-specific questions, it will be necessary to obtain new data through monitoring. Potential data needs include: filling gaps in emissions inventory data; providing input data for models and validating modeling results; generating new data to more fully characterize exposures in areas, populations, or pathways; establishing trends over time; or supplementing a body of data to increase their quality for the risk management decision. The process for itemizing data needs includes articulating critical decision criteria (which may drive data quality needs and/or selection of specific methods), applying these criteria to determine areas where existing data are insufficient, and identifying the manner in which new data can supplement existing data to meet the decision criteria. In many ways, the identification and enumeration of data needs acts a bridge between the conceptual model and the DQO process.

4. **Define data quality needs**. The reliability (e.g., accuracy and precision) of monitoring results must be adequate to meet the needs of the risk management decision. However, given finite resources, even well-designed studies may not be able to achieve all quality criteria. That limitation makes it important to determine which criteria are essential for addressing the

study-specific decision problem and for focusing resources on meeting (and not necessarily exceeding) those criteria.

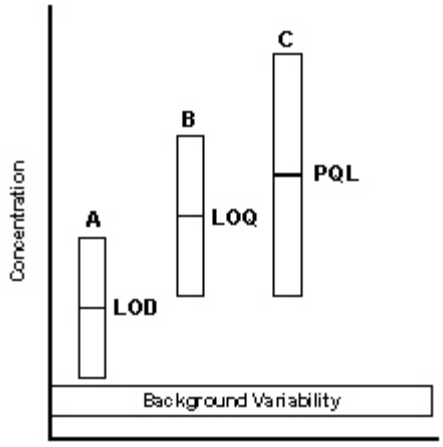
The DQO process determines general data quality objectives to meet specific needs. This process can be informed both by a well specified decision statement and by a sensitivity analysis to determine which aspects of a full monitoring program will require the greatest attention and resources to support that decision. Identification of data quality needs at this level is targeted on the specific problem identified in Step 1, but is independent of the specific methods to be applied. It is important to base data quality criteria at this step on what is required to answer the problem identified in Step 1, not on impressions of best available analytical methods, approaches used in the past, or consideration of questions that might be of general scientific interest but are not of direct use in the decision problem. A common approach is to consider all aspects of sample and data handling from collection to data report writing, as these affect the confidence with which decisions can be made through the introduction of random or systemic errors. A number of factors affect data quality, including bias related to sampling error (e.g., taking only a single sample at one location, which may or may not be representative of actual ambient concentrations) and relative precision related to analysis methods.

5. **Select monitoring methods to meet data quality needs**. The choice of monitoring method depends on the scale of the assessment, specific contaminant(s) to be analyzed, the sampling time over which the result is derived (e.g., a sample collected over 15 minutes versus a sample collected over 24 hours), the decision criteria or other reporting limit needs, and the resources available (see Section 10.3). Methodologies include the sampling methods and techniques, sampling program design (i.e, sampling frequency, coverage, and density), as well as analytical methods. The data quality needs identified in Step 4 represent the total data quality requirements of all aspects of the sampling and analysis process necessary to support risk-based decision-making. Therefore, evaluation of all aspects of sampling and analysis with respect to data quality needs is necessary for proper method selection.

   The QAPP process involves balancing decisions for method selection to meet data and quality needs. Selection of the methods for both sampling and data analysis defines the approach and defines what is termed the **measurement quality objectives**. Although there is a natural tendency to select sampling and analysis methods based on previous data, it is important that the benefit of consistency and likely improved comparability are not outweighed by data gaps that Step 3 identified. For example, in a risk assessment for chlorinated volatile solvents, the presence of fluorinated volatile solvents may cause assessors to overestimate chlorinated concentrations due to analytical interferences. The method selection generally takes into account the known or suspected presence of other chemicals having similar toxic effects, symptoms, and mechanisms, and/or that which otherwise may affect sampling and analysis results. To take this into account, the study may require adding chemicals to the target analyte list, selecting a method where these compounds are not potential interferents, or limiting the scope of the study with stated assumptions about contributions from these undefined factors (e.g., stating only that the measured concentration is the sum of a defined set of analytes and not applicable to any one analyte in the mixture).

Detection Limits and Limits of Quantitation

The **detection limit** is the minimum concentration that an analyst can reliably expected to find (i.e., detect) in a sample, if it is present. For any given method (e.g., the method to analyze for volatile organic compounds [VOCs] in air), this limit is established in each lab for each instrument and is called the **method detection limit** or **MDL**. An MDL of 1μg/m^3, indicates that a field sample that contains 1 μg/m^3 or below of contaminant will probably not be detected by the instrument in question. The **limit of quantitation (LOQ)**, on the other hand, is the minimum concentration for which the analyst can reliably say that the substance is present in the sample and at a specific concentration within some pre-established limits of precision and accuracy. If the limit of quantitation is 2 μg/m^3, then measurement results above 2 μg/m^3 may be reported as not only indicating the presence of the substance in the sample, but as indicating the specific concentration measured (i.e., positive identification, certain concentration). Measurements between the MDL and the LOQ , indicate the presence of the substance in the sample, but analysts can only make an estimate of the concentration (i.e., certain identification, uncertain concentration). NOTE: It is common (but incorrect) to refer to the quantitation limit as the detection limit. The LOQ, practical quantitation limit (PQL), estimated quantitation limit (EQL), and sample quantitation limit (SQL; see below) are all limits of quantitation, not detection. Thus, when one says "benzene was not detected at a detection limit of 5 μg/m^3," this most likely actually means "benzene was not detected; the limit of quantitation was 5 μg/m^3." Likewise, when a lab reports a measurement as "<5 μg/m^3," this most likely means "not detected; the limit of quantitation was 5 μg/m^3." There is much confusion on this point and analysts must clarify with the laboratory exactly what they mean in their lab reports (and what the analyst needs to have reported to them for their risk assessment activities). For air toxics risk assessments, the MDL is largely irrelevant for purposes of estimating exposure and the limit of quantitation is the critical information that needs to be reported (see Chapter 7).



In establishing limits of detection and quantitation, it is necessary to give the confidence level associated with the detection limit and the limit of quantitation. In this figure, the confidence level is 99 percent. The *Limit of Detection* (LOD) is then the minimum concentration that has a 99 percent probability of producing a result above background noise (background is shown in the figure as a horizontal bar) using a specific method. The LOD includes two considerations: an *instrument detection limit*, accounting for variation in the instrument when it is presented with repeated samples at the same concentration, and additional variation caused by the need to sample, handle the sample, etc. (which can cause variations in the relationship between the concentration in the environmental medium and the concentration presented to the instrument). The LOD is the horizontal line in the bar marked A. Note that the range of variation of results from a concentration at the LOD (shown as the bar marked A), and the lower end of this range just barely avoids moving into the range of background variability.

Detection Limits and Limits of Quantitation (continued)

The LOQ assumes best practice in performing the measurements. It also is of interest to ask what the LOQ would be using more common, routine practice. The *Practical Quantitation Limit* (PQL) is the minimum concentration that has a 99 percent probability of producing a result above the LOD under routine lab conditions (shown as the bar marked C). Under these conditions, the variation will be larger than under ideal conditions, and so the PQL is higher than the LOD. Each lab must establish these parameters for each method on each analytical instrument. When actual environmental samples are evaluated on an instrument, the actual PQL reported for any given sample may vary (for example, if a sample is highly concentrated and needs dilution before analysis, the resulting PQL for that sample will be elevated by an amount proportional to the dilution). It is for this reason that PQLs reported for actual samples are referred to as a **sample quantitation limits** or **SQLs**. When using analytical monitoring data for air toxics risk assessment purposes, ***the MDL is irrelevant***. The SQL is the key factor in developing exposure concentrations (see Chapter 7).

Having established these terms, some system then is needed to "flag" results as being either usable or unusable for the purposes of decision-making. For example, in the Superfund program,[(a)] results are flagged "*R"* if the data are unusable for some reason and *"J"* if the data fall between the SQL and the MDL. A more thorough description of data qualifiers if presented in Appendix I.

[(a)]U.S. Environmental Protection Agency. 1992. *Guidance for Data Usability in Risk Assessment (Part A)*. Office of Emergency and Remedial Response, Washington, D.C. EPA Publication 9285.7-09A; available at http://www.epa.gov/superfund/programs/risk/datause/parta.htm.

6. **Develop systems to ensure that data meet decision requirements**. Setting the objectives and selecting sampling and methods capable of meeting the DQOs are the prelude to determining whether and to what degree the data may support risk management decisions. Having collected and analyzed the data, it will be necessary to determine whether decisions can now be made with the desired confidence. For example, the actual data collected must be assessed for quality and compared against any decision criteria such as toxicity dose-response values. Where the quality is insufficient to support the decision (e.g., insufficient to determine whether the benchmark is or is not exceeded), the previous steps may need to be re-assessed.

   It is also important to evaluate the contribution to uncertainty that is related to sample collection and sample program design as well as analytical method uncertainty. Sampling uncertainty is decreased when sampling density increases, however resource limits often constrain sample density. Typically, errors in the collection of field samples are much greater than errors introduced by preparation, handling, and data analysis; yet, most sampling studies have devoted resources to assessing and mitigating laboratory errors. Ultimately, the proper use of a QAPP that considers the entire process (sample collection through lab data reporting) allows for evaluation of and reduction in uncertainty across all the activities of the monitoring program, focusing resources on those aspects contributing most significantly to uncertainty affecting decision-making.

7. **Develop documentation**. The QAPP and other planning documents must record the results of the environmental data collection design process. Information to be documented includes the assumptions, findings, outliers, biases, data confidences, and other factors that are critical to implementation, as well as evaluation and eventual interpretation of the data collected. Data collected and analyzed is often reviewed thoroughly to ensure they are adequate to support decisions; sufficient documentation allows such a review.

10.4.2 Specific Planning Issues

The design of the monitoring program also raises some specific issues:

- **Select appropriate monitoring or sampling methods for the chemical(s) to be measured**. In general, it is important that the methods selected have the sensitivity needed to monitor at concentrations likely to be of health and/or regulatory concern. At a minimum, the PQL or SQL should be below any relevant health benchmarks (e.g., the human health dose-response values discussed in Chapter 12). For some chemicals, the limit of the current technology may not allow for a PQL or SQL that is below a health benchmark (or, that level may be reached, but at a higher cost). In such instances, the planning and scoping team must decide how best to balance resources to support data quality needs.

- **Select appropriate monitoring sites, sample collection frequency, and length of sampling time for the spatial and temporal variation of the scale being assessed and for the objective of the air toxics monitoring being conducted**. The way monitoring captures this variation depends on the particular measure(s) needed to support the risk management decision. For example, the monitoring goal might be to estimate the average long-term exposure to people spread over a large geographic region (e.g., the average urban exposure for a typical resident in a town). In this case, measurements spaced on a grid throughout that region, or selected with a spatial density proportional to population density, may be appropriate. On the other hand, if the goal is to identify or verify the maximum modeled exposure or to perform a screening-level assessment in a population living down-wind from an industrial source, sampling should be performed at the location likely to represent the highest exposure, or in several different regions to identify the site representing the highest exposure. Again, issues such as atmospheric photochemistry and differential settling of metals are important considerations.

  Assessors often make similar decisions when considering temporal variation. For example, samples may vary over time due to fluctuations (e.g., emission rates from a facility may fluctuate over time) or a systematic temporal trend (e.g., a facility might change its production methods or products over time). In the former case, it is necessary to obtain enough samples spread over a large interval of time to estimate the mean over the measurement interval. In the latter case, the samples must be spaced in time so as to capture the trend (i.e., a **time-trend study** must be performed). In addition, the objective of a study may be to capture high short-term spikes in chemical concentrations. In this case, samples collected over a 24-hour period may "dilute out" these spikes, and frequent shorter term samples (e.g., collected over 15 minutes) may be required.

A recent evaluation of many of the issues regarding variability was recently published using data from a wide range of monitoring sites throughout the United States (see also Exhibit 10-4).[5] These results support the conclusions that: (1) environmental variability is a more important source of uncertainty than analytical uncertainty, emphasizing the need to carefully select the location and timing of monitoring; (2) temporal variability dominates data variability, emphasizing the need to not only carefully select the timing of monitoring, but to ensure that results are properly averaged over relevant exposure periods; and, (3) analytical uncertainty becomes a more significant contributor to overall uncertainty as ambient concentrations approach background levels.

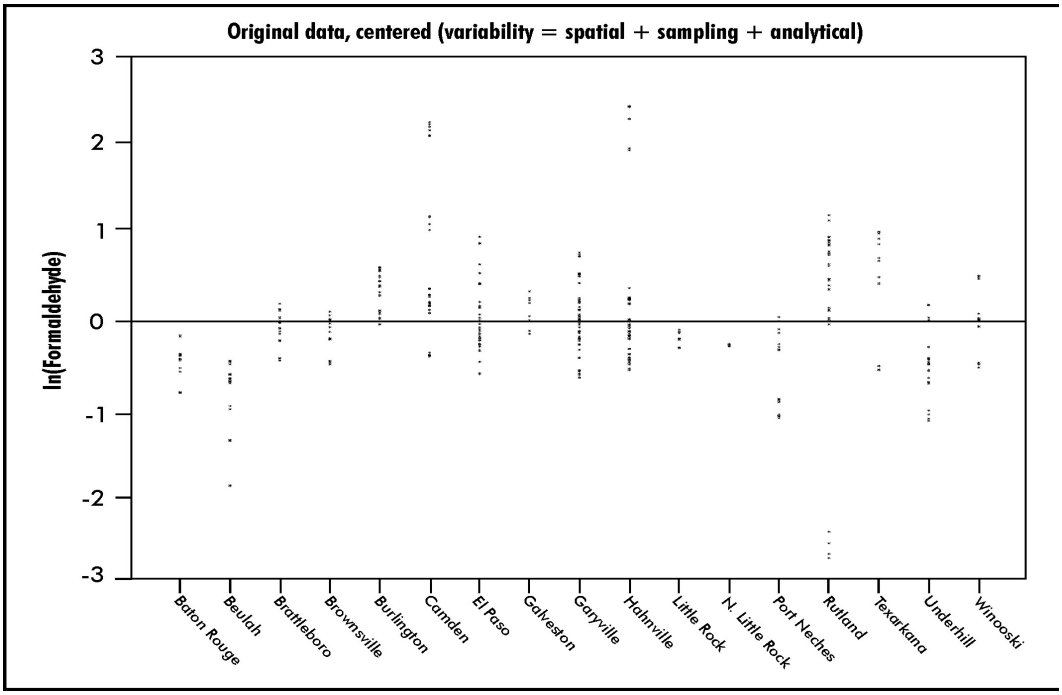
- **Most often, the monitoring efforts address the four main sources of variability in measurements**. These four sources are:

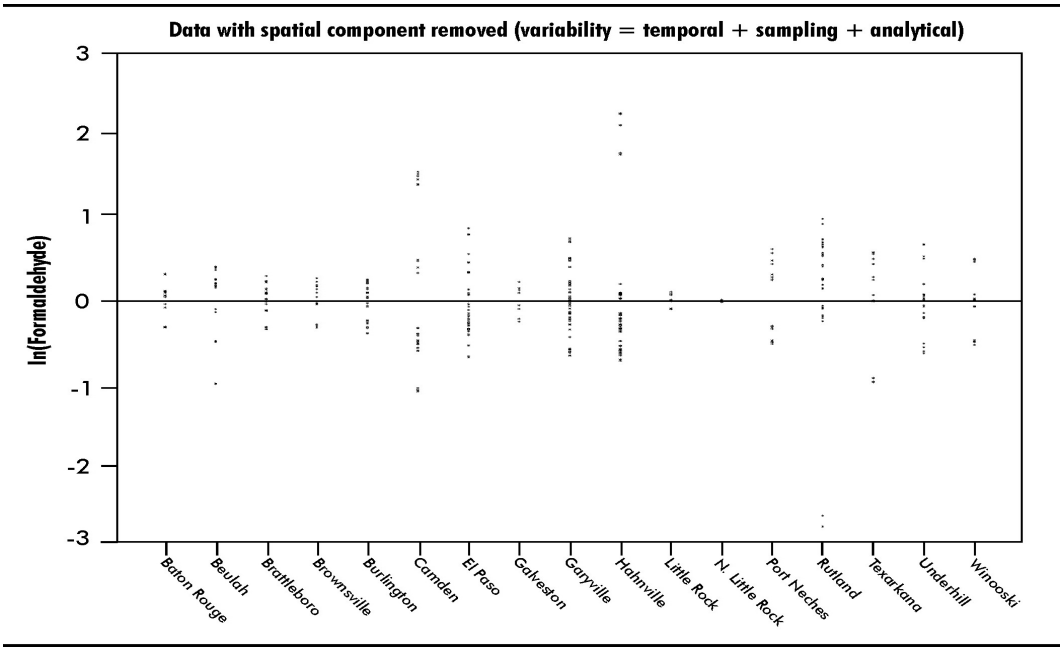
  - **Analytical**. The same sample analyzed repeatedly yields different concentrations.
  - **Sampling**. Duplicate samples collected using two identical monitoring devices from the same location and time yield different concentrations. This type of duplicate sampling is often performed to determine the precision of the method. In general, a minimum of 10 percent of the measurements in a monitoring program should be co-located to collect duplicate samples.
  - **Temporal**. Repeated samples at different times at the same location yield different concentrations.
  - **Spatial**. Samples from different locations at the same time yield different concentrations.

  Ideally, assessors allocate monitoring resources in a manner that is consistent with the relative contribution of these four sources to uncertainty. However, uncertainty may not be evident prior to establishing the sampling program. Some insights on the relative contributions can be obtained from the recent study of monitoring variability,[5] but it generally will be necessary to perform an analysis of the analytical uncertainty, the precision, and the degree of spatial and temporal variability before a firm judgment of the relative contributions can be made.

  As noted previously, ambient air monitoring data may not provide a completely accurate picture of exposure. There are several reasons for this limitation. First, air toxics monitors usually are physically located to provide an estimate of air concentration at a specific location. The assessor must then determine how representative the results are to populations in the geographic area around the monitor. For some chemicals, monitoring results can be reasonably representative, especially if the concentration does not show high levels of spatial variability. For other chemicals, results may not be very representative at all, especially at some distance from the monitor. In addition, because people move around outside, their exposures are an average of the ambient air concentrations over the geographic regions in which they move; this exposure may not correspond to the average at any particular monitoring location. People also receive protection from the ambient environment, either in vehicles or by moving indoors or through filters. Thus, ambient air concentrations measured through monitoring and analysis can be taken as an indication of the potential for exposure at a given location.

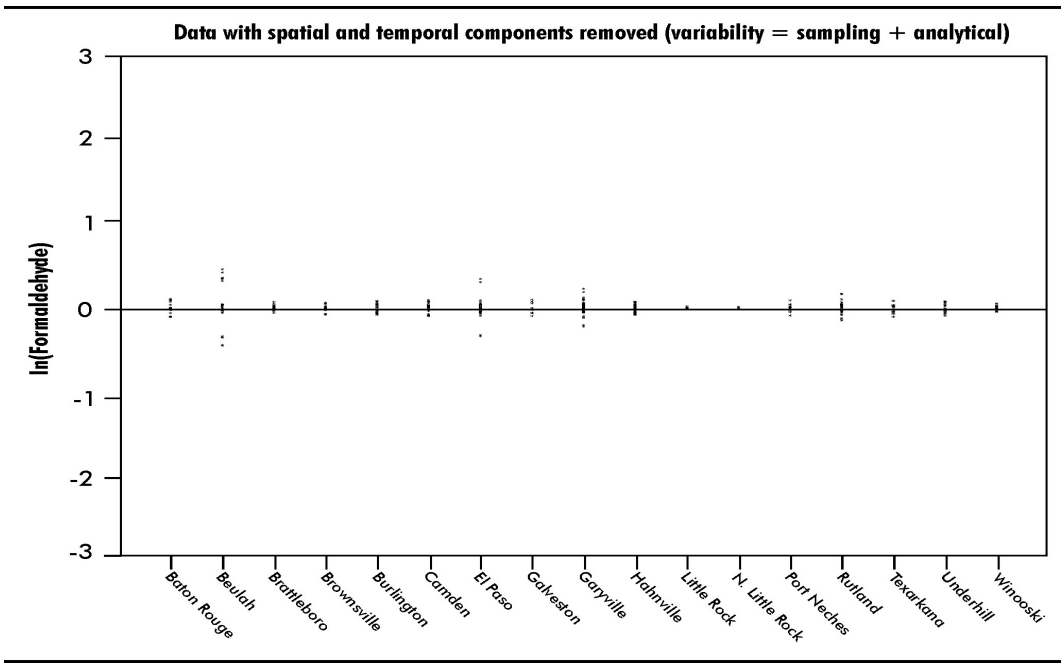
Exhibit 10-4. Temporal and Spatial Sources of Variability in Formaldehyde Sampling

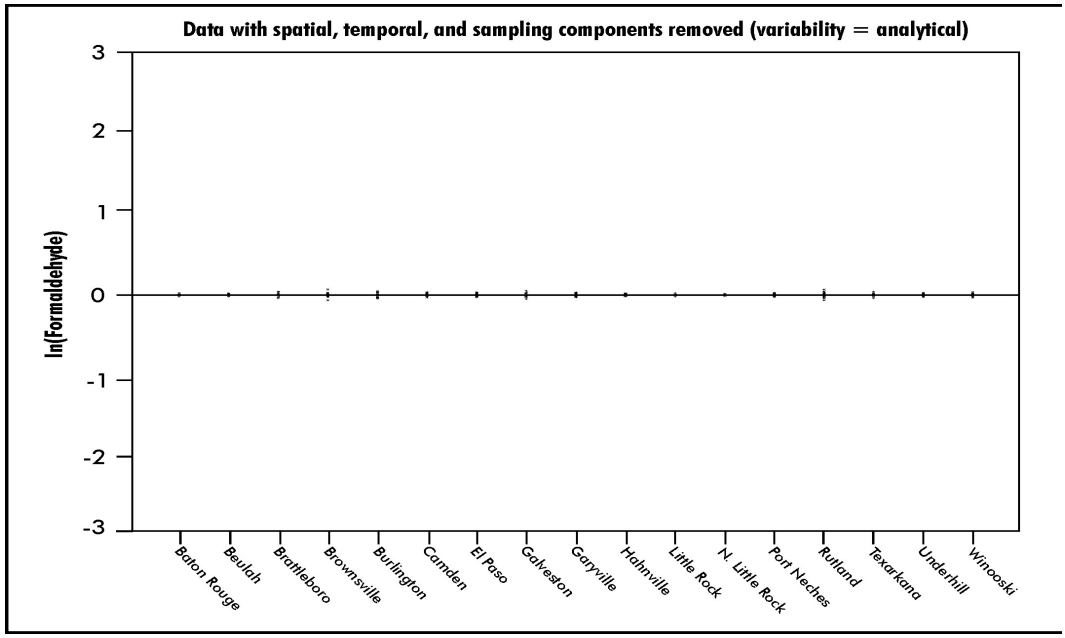




The four graphs in this exhibit summarize the results of Bortnick and Stetzer,[4] obtained by sequentially removing sources of variability. Note that the analytical variability is the smallest source of variability in this case, followed by sampling variability and temporal/spatial variability. Clearly in

Exhibit 10-4 (continued)





this case, a choice of sampling focused on temporal and spatial contributions to variability is needed; since temporal variability dominated, primary attention would focus first on that component in each sampled geographic region.

- **Follow and define standard operating procedures**. Risk assessors follow and define standard operating procedures both in the field (during sample collection and transport to the laboratory) and in the laboratory (during sample analysis). Procedures include those related to sample collection, sample transport, sample storage (including prevention of sample degradation), and chain of custody procedures, as well as sample analysis, validation, and data reporting. Procedures to identify potential problems are put in place. Periodic audits (both field and lab) are commonly performed to ensure procedures are being followed and that measurement and analytical devices are working properly.

- **Determine quantitation and compare limits**. A common approach is to determine quantitation limits and compare them against relevant decision needs, including health benchmarks and likely environmental levels. These quantitation limits should be below the health benchmarks and environmental levels to provide data of use in risk-based decisions.

- **Properly calibrate measurement processes**. One way to ensure the accuracy of the method is to properly calibrate measurement processes. To accomplish this, assessors perform calibration on a time schedule shorter than the time needed for the equipment to "drift"[(b)] further than is permitted under the criteria of accuracy and precision. It is for this reason that it is essential that systems be re-calibrated periodically, on a schedule that is related to the data quality objectives. In addition, it is desirable to cross-calibrate measurement methods by comparing results from several individuals and labs. In an inter-laboratory comparison, split and duplicate samples are submitted to several labs simultaneously, the results are collected, and variation between labs are assessed. Ideally, sample analysis in a monitoring study would be conducted at a laboratory that has participated in such an inter-laboratory comparison and has been certified to produce results within acceptable data quality limits.

- **Adequately record and archive results**. The best monitoring program can fail due to improper record-keeping. A periodic, random check of the archived records (e.g., computer files) is commonly made against "hard copies" to ensure the integrity of the process of recording the data. The recording of all results, including a description of the QA/QC and Data Quality Indicators, is essential because risk managers will use the results in their decisions.

- **Match measurement intervals to the relevant modeling assumptions or health endpoints**. Different health effects require varying averaging time-periods. Cancer and other chronic effects generally require averages over relatively long periods such as a year or more (up to a lifetime). In this case, samples may be taken randomly or systematically throughout the year, with the criterion of obtaining an accurate estimate of the mean. Acute effects, however, require an understanding of the temporal variability over short periods of time. For example, monitors need to measure benzene concentrations within shorter time intervals (e.g., 15 minute, one-hour, 24-hour) for comparison with a health benchmark reflective of the same time period.

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[b] "Drift" refers to the fact that monitoring systems that are calibrated generally change their electronic and other characteristics in time, so the calibration factor also changes in time.

- **Ensure that temporal sampling reflects diurnal (time-of-day) and seasonal variability**. It is important to recognize that source terms and meteorological conditions can vary systematically both over a day and throughout the seasons. Monitoring programs commonly reflect this pattern, providing proper averages throughout a day (by sampling at selected time points in a day) and between the seasons (by sampling in the different seasons).

In general, most monitoring schemes that are designed to attenuate and validate a model will collect samples and analyze a relatively short list of "indicator compounds." If attenuation and validation are the primary motivation for sample collection, it may not be necessary to measure every compound being modeled, as long as it can be assumed that unmodeled compounds would be expected to behave similarly. However, the amount and type of data collected in the monitoring program designed to validate predicted model results should match the assumptions of the modeling program. For example, if the goal of the modeling program is to estimate long term (usually annual average) concentrations, then monitoring data must also be collected in sufficient quantity to develop an annual average value to compare to the model results. (In general, monitoring samples collected every six days for a year are required to develop a stable estimate of annual average.)[2]

10.5 Implementing Air Toxics Monitoring

Implementing a monitoring program raises two issues in addition to the items above that relate to planning for a monitoring study. These include selecting the actual location of monitors and selecting methods for data analysis and reporting. Each is discussed in a separate subsection below.

10.5.1 Locating Monitors and Selecting Sample Size

Determining the location of an air toxics monitor depends on a number of factors, including the specific purpose of the monitoring (e.g., confirm modeled concentrations at a specific location, estimate background concentrations), meteorological and terrain constraints, and the relative magnitude and location of the source(s) of concern versus other emissions sources that might contribute to measured air concentrations. For example, locations too close to a source may underestimate exposure concentrations if the plume has not yet reached ground level where people can come into contact with the contaminants. Locations too far from the source may also underestimate exposure concentrations for large groups of people due to the dispersion that takes place between the point of touch-down of the plume and the point of monitoring.

10.5.1.1 Locating Monitors

EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems*[6] provides a set of consistent QA practices that will improve the quality of the nation's ambient air quality monitoring data and ensure comparability among sites across the nation. Although these practices were developed specifically for criteria air pollutants, they provide useful guidance for air toxics risk assessments. Exhibit 10-5 summarizes some of the *Handbook's* guidance on the relationship between topography, air flow, and the location of monitoring locations. The following factors are usually considered when siting monitors:

- **Perform measurements at locations that are representative of exposure**. Determining the location will depend on whether the goal is to quantify exposures in general, or exposures to the maximally exposed individual. In the latter case, locations too close to a source may underestimate exposure if the plume has not yet reached ground level where people can come into contact with the contaminant. Locations too far from the source may also underestimate exposure to large groups of people due to the dispersion that takes place between the point of touch-down of the plume and the point of monitoring. Exhibit 10-3 above presented an example of this issue. In that hypothetical example, the area of maximum concentrations predicted by the air quality model falls somewhere within the area bounded by grid points 2, 4, S1, and S3. If the goal of monitoring is to verify these maximum concentrations, then the ideal location for the monitor would be on the plume centerline at the exact point of touch-down of the plume. However, if the goal of monitoring is to verify maximum concentrations at the point of actual exposures, location at the site indicated in Exhibit 10-3 may be more appropriate (measurements at the point of plume touch-down may overestimate maximum actual exposure if there are no individuals within that area). It is essential to determine whether monitoring will estimate exposures to existing individuals or to hypothetical individuals who might move into currently unoccupied areas.

Exhibit 10-5. Relationships of Topography, Air Flow, and Monitoring Site Selection

Station Category	Characterization
A (ground level)	Heavy pollutant concentrations, high potential for pollutant buildup. A site 3-5 m (10-16 ft) from a major traffic artery that has local terrain features restricting ventilation. A sampler probe that is 3-6 m (10-20 ft) above ground.
B (ground level)	Heavy pollutant concentrations, minimal potential for a pollutant buildup. A site 3-14 m (15-50 ft) from a major traffic artery, with good natural ventilation. A sampler probe that is 3-6 m (10-20 ft) above ground.
C (ground level)	Moderate pollutant concentrations. A site 15-60m (5-200 ft) from a major traffic artery. A sampler probe that is 3-6 m (10-20 ft) above ground.
D (ground level)	Low pollutant concentrations. A site $\geq$ 60 m ($\geq$ 200 ft) from a traffic artery. A sampler probe that is 3-6 m (10-20 ft) above ground.
E (air mass)	A sampler probe that is 6-45 m (20-150 ft) above ground. Two subclasses: (1) good exposure from all sides (e.g., on top of a building), or (2) directionally biased exposure (probe extended from a window).
F (source-oriented)	A sampler that is adjacent to a point source. Monitoring that yields data directly relatable to the emissions source.

Source: Table 6.5 of EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems*[6]

When source location is the goal of monitoring, the siting of a monitor depends on the meteorological conditions and the spatial locations of suspected sources. Again, the hypothetical example in Exhibit 10-3 provides some insights. If the source is suspected to be at the center of the geographic area, and if the wind direction is predominantly towards the east (as it is in that example), the monitor or sampler would be located to the east of the source and operated both at times when the wind blows towards the east and when the wind blows in the opposite (or another) direction. Support for the claim that the source is located

at the origin, and dominates exposures in the area around the monitor, would then be strongest if the ambient concentration increases significantly when the wind blows towards the east and drops significantly when it blows in other directions. If the data did not indicate this effect, then the source is not at the center, or there is an additional, and perhaps more significant, source in the area.

- **Take into account shielding and concentrating effects.** Buildings, hills, and trees can have shielding and concentrating effects. These effects may cause assessors to underestimate exposure if either measurement sites are shielded from normal air flow or if these same structures produce high concentrations downwind due to lee effects. Unless there is a pattern of movement of people that make sites near buildings and other structures of particular interest, assessors should perform measurements away from the influence of these structures. It is particularly important to locate monitors away from such structures if the goal is to locate sources, as the flow patterns for air are highly complex near these structures, greatly complicating the ability to identify the source location from monitoring data.

- **Be aware that sources of air toxics from mobile sources (cars, trucks, etc.) can complicate measurements of ambient air concentrations produced by stationary sources**. For the estimates of exposures from stationary sources, it may be preferable to make measurements at locations away from roads. Monitoring should occur at distances ranging from 3 to 61 meters from a major traffic artery (see Exhibit 10-5). These roads provide, in a sense, a "background" level, or noise, above which the source must rise to create a discernible signal. Of course, if total ambient exposure from all sources is to be estimated, and the exposed population spends a significant fraction of time near roads, this factor may be captured by selecting a sample of sites near those roads.

- **Make sure that the heights of monitoring and sampling devices are consistent with the breathing zones of people when public exposures are being evaluated**. This is generally between 1 and 2 meters (the lower end being for children and the upper end for adults). While less important for highly dispersed gases (i.e., gases with high diffusion coefficients), this consideration can be important for heavy gases and particulates, which produce significant vertical gradients of concentration.

- **Keep in mind that background concentrations can be difficult to determine**. Although background concentrations can be difficult to determine, it is important to estimate this factor as accurately as possible at the location of measurement (see below for a discussion of background concentrations). Unfortunately, even background levels can vary dramatically over time and over a geographic area, and so assessors should exercise caution in using past studies and studies from other geographic areas in establishing background for a measurement location. Meteorological and pollutant source information must also be carefully considered in selecting an appropriate background monitoring location. The location must not be near major sources of the contaminant, or in the predominant down-wind direction of those sources. The number of background samples should be determined during planning/scoping/problem formulation stage, and be based on statistical testing criteria specified in the DQOs.

The choice of monitoring or sampling locations depends on the spatial scale of the assessment being supported by the measurement program (i.e., micro, middle, neighborhood, urban, regional, or national). Note that samples collected (generally) at the micro-scale, middle-scale, or neighborhood-scale for the specific purpose of determining the impact of a source or co-located groups of sources on a specific population are called **source-oriented monitoring samples**.

In each case, selection of sites for the monitoring program should consider whether:

- A **mean value** is needed for a region (in which case, the sampling must be sufficient to allow interpolation of a surface concentration across that region, from which a mean may be estimated, or a mobile monitor/sampler must be used while moving throughout the region).

- A **mean value** is needed for an area. In this case, the monitor would be placed so as to capture the average of all the sources in the area (i.e., it is usually not oriented towards one source).

- A **maximum value** is needed (for example, for a screening assessment or an estimate of the maximum exposure to an individual from a particular source or co-located groups of sources; in this case, the task is to identify a location as close as possible to this point of maximal exposure).

- A **distribution of exposures** across the population in the region is needed, in which case sampling might be performed across a region. Information on the number of monitoring stations needed to perform this analysis with an acceptable level of accuracy/precision was recently evaluated and discussed by the Lake Michigan Air Directors Consortium (http://www.ladco.org/toxics.html).

- A **test of a model** is being conducted (in which case the location is selected to provide the most meaningful and unambiguous test of the model predictions under established source term and meteorological conditions).

In all five cases above, it is important to determine compounds that might interfere with the measurement of target compounds and, to the extent feasible, locate sampling devices in areas where such interference is small (without compromising the need to cover a geographic region). It also is important to establish one or more "background" and/or "control" locations so the elevation of concentrations or exposures at sampling locations due to sources not located in the assessment area can be determined.

In each case, site selection can improve through use of release data (source terms) and dispersion models. An accurate estimate both of average exposures and distributions of exposure (i.e., concentration measured across different monitors) generally will require adequate sampling in geographic regions characterized by the highest concentrations in addition to sampling in less impacted areas. Since such regions may represent a small fraction of the area in the overall study region, it may be necessary to "over-sample" in the highest exposed areas to ensure the points of maximal exposure are not missed. This process might be accomplished, for example, by sampling on a grid, with the grid density higher in the area surrounding the suspected point of maximal exposure; this will be particularly important if initial monitoring/sampling indicates high spatial variability in the area around the point of maximal exposure. For example, regions

near known, large emissions sources, and downwind of the predominant wind direction, should probably receive increased attention in sampling if a distribution of concentration is being developed across a larger assessment area. If samples were taken only in relatively non-impacted areas, the resulting distribution might not reflect the actual exposure of many area residents. (Ultimately, this is one of the prime reasons for using modeling to evaluate exposure; namely, that models can estimate exposure concentration at as many geographic points in a assessment area as the analyst wishes and for which sufficient emissions inventory data and computing power are available. Thus, modeling obviates these monitoring concerns.)

Background and Control Samples

Background monitors are monitors that are place in the predominant upwind direction (relative to sources) in the assessment area to measure the concentrations of the COPC in air that is moving into the assessment area. The results of such monitoring is helpful in understanding the monitoring results obtained in the assessment area; however, background monitoring results should not be subtracted from assessment area monitoring results because of the uncertainties in the background monitor as a truly representative measure of long term ambient background concentrations. Instead, EPA recommends bar charts that compare contemporaneous concentrations of a chemical in a background monitor to the same chemical at assessment area monitors; these charts provide a sense of the potential influence of background concentrations on the assessment area.

Unlike a background monitor, which is located upwind of the assessment area, a **control monitor** is located within the assessment area and is sited in such a way as to determine the average concentration of all pollutant sources, once mixing has occurred (including chemicals blowing into the assessment area from outside sources, mobile source emissions, and stationary source emissions within the assessment area). Control monitors should be located away from direct influence of any one or group of sources in the assessment area. Similar to background monitoring results, control monitor results should not be subtracted from other assessment area monitoring results (or modeling results). Instead, a simple bar chart comparison is usually adequate to compare the general "urban soup" to more focused monitors.

For the case of model testing, random sampling is not required or even desired. Instead, sampling is performed specifically in one or more locations where the conditions of emissions and dispersion are well established, and where there are no interfering sources or compounds. An ideal situation is a single, known source and a stable wind pattern during the period of sampling. Even in such cases, however, it will be necessary to provide a sampling grid covering the plume dimensions, since small errors in assigning wind direction can result in significant differences between model results and measurements. By sampling at a variety of locations in the plume, it is possible to adjust the model to determine whether a better fit might be obtained by more accurate information on the wind field, effective stack height, and other parameters.

As part of the national-scale assessment component of the 1996 National-Scale Air Toxics Assessment (NATA) activities, EPA compared monitoring to modeling results by using selected locations and compounds (seven HAPs) throughout the U.S. (see www.epa.gov/ttn/atw/nata/mtom_pre.html). The comparison goal was to assess the closeness of modeling and monitoring results, which would expose the overall uncertainty in estimating exposures. They found, for example, that modeled results generally underestimated results at monitors when the modeling was performed to predict air concentrations at the precise location

of the monitor; however, results were more comparable when the maximum concentration that the model predicted was compared against the maximum monitor concentration, without the requirement that modeling and monitoring be at the same location. These results indicate that uncertainties in the modeling produced errors that shifted the location of the point of maximal exposure, but not necessarily the magnitude of maximal exposure. A significantly more detailed uncertainty analysis currently is underway, with results expected in 2004 (these will be available at the NATA website).

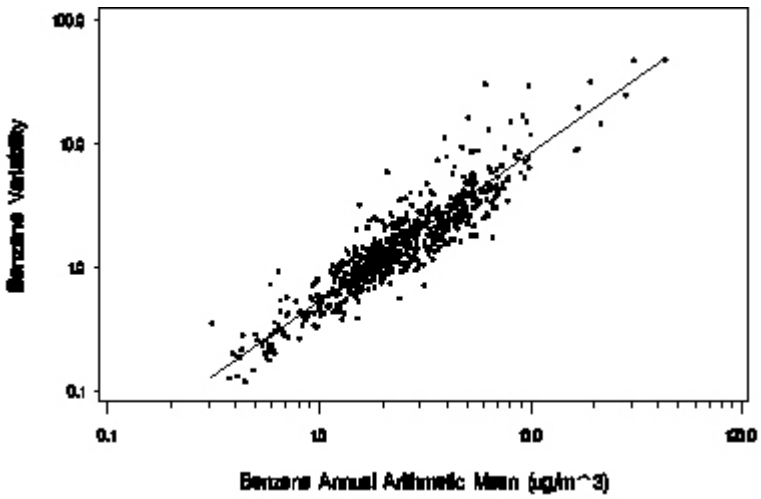
10.5.1.2 Selecting Sample Size

With respect to determining the quality of any estimates of mean concentration or exposure at a location, the coefficient of variation (CV) should be calculated to determine the number of samples needed to meet DQOs established by the decision problem. If σ is the standard deviation of a set of N measurements performed randomly throughout a geographic region and randomly in time, and μ is the mean for that sample set, the value of CV is:

$$CV = \frac{\frac{\sigma}{\sqrt{N}}}{\mu} \qquad \text{(Equation 10-1)}$$

The target value of CV depends on the decision criteria establishing the needed accuracy of an estimate of concentration or exposure, but a general target of less than 0.5 (50 percent) is suggested and a value of 0.2 or less should be possible. (This discussion assumes that the samples are representative of the geographic area and time period for which the average is being calculated.)

The above calculation of CV requires knowledge of σ and μ, which can only be obtained after the sampling program has been underway. It is possible, however, to estimate σ from an initial guess of the mean concentration or exposure, μ, through regression functions such as those established by Bortnick and Stetzer.[5] An example of such a regression is shown below based on a scatter plot of data from benzene monitoring.



Note that σ increases as μ increases. The authors use a lognormal relationship between σ and μ:

$$\ln \sigma = \ln a + \ln \mu \quad or \quad \sigma = a\mu^2 \qquad \text{(Equation 10-2)}$$

They perform a weighted least-squares regression (solid line in the figure above) and obtain for the case of benzene:

$$CV = \frac{\frac{0.54}{\sqrt{N}}}{0.2\mu} \qquad \text{(Equation 10-3)}$$

The approximate size of N needed to produce the desired value of CV may then be estimated from the above equation if an estimate of μ is available from either past monitoring data, similar geographic regions, or models.

10.5.1.3 Setting Up a Monitoring/Sampling Program

While the design of a monitoring program will depend in many ways on the kind of monitoring to be conducted, there are some general aspects of all monitoring programs that assessors should consider. EPA guidance describes many of these issues in detail.[7]

The general aspects related to designing a monitoring program that supports risk assessment are developed and written down in the planning, scoping, problem formulation phase (particularly, much of the following information is included in the study-specific conceptual model and the analysis plan and QAPP for monitoring activities). This activity involves three steps: (1) identify the sources, including the contaminants, the concentrations, the timing and locations of releases, as well as the hypotheses you want to test (e.g., whether a source exists, its relative contribution to overall exposures, etc.); (2) determine the exposure pathways (which in the case of air monitoring is inhalation and perhaps dermal absorption through immersion in air); and (3) determine the receptors of interest, including any sensitive subpopulations, their locations, how they are exposed, and relevant health benchmarks (e.g., IURs or RfCs). The conceptual model can be used to identify where significant exposures are likely to occur to receptors of interest, which in turn helps to guide the selection of monitoring sites. The following steps are then often used to develop, conduct, and evaluate the results of monitoring:

1. Collect and review existing air monitoring information for the site. This information should include data on concentrations, sources, locations of receptors, and other environmental data (e.g., meteorological data) needed to guide decisions. The sources of these data will depend on the location of the site, but a good start is to consider results from some of the national monitoring networks.

2. Determine the level of sophistication needed by the monitoring program. This level is established in the QAPP and the DQOs. The sophistication might range from simple screening procedures (e.g., to determine whether there are any exposures of concern) to more sophisticated methods intended to develop accurate maps of exposure across the region.

3. Develop a clear air monitoring plan, including determining the following: types of air monitors (these depend on the compounds identified as being of interest); the number and

location of monitors; the frequency and duration of monitoring, sampling and analysis of samples; and any QA/QC procedures that must be in place to meet DQOs.

4. Develop a detailed, written plan for day-to-day activities related to how equipment will be maintained and calibrated, and how to document results and QA/QC procedures. The data maintenance plan should include development of a system of logbooks for entering data, along with procedures to ensure the data are entered correctly and the logbooks are archived. There should be a clear procedure for maintaining chain-of-custody for both the samples and the logged results.

5. Evaluate the air monitoring results for their validity and reliability, including summary indicators of data quality (e.g., the data qualifiers discussed elsewhere in this chapter), and summarize these results so decision-makers can understand this quality and ensure the quality meets decision needs. This evaluation should include a summary of the statistical procedures used and the air concentration results, and an estimate of uncertainty in results deemed usable by the analyst (including uncertainty due to monitoring equipment, handling of samples, and sample analysis).

There are a number of specific issues that arise in Step 3 above that relate to the development of the monitoring program. These issues are summarized here in roughly the order in which they would be approached in developing a real program:

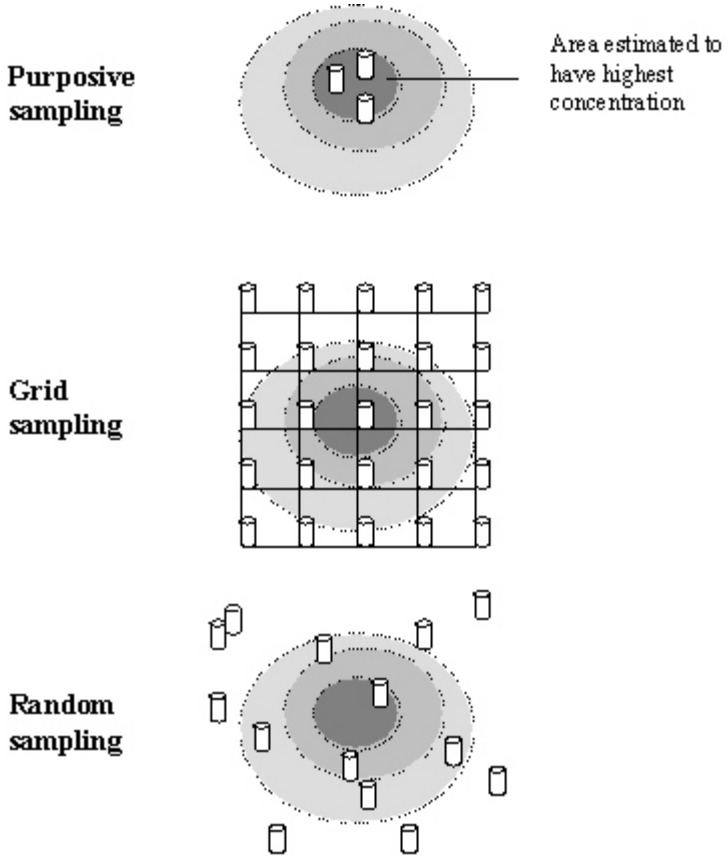
- **Establishing sampling locations**. Sampling may be purposive, random, or systematic. Purposive sampling refers to locating the monitor at a particular location because that location is of special interest. While such sampling can be useful to address specialized questions (such as the impacts of a specific source, or the reliability of model results), they generally are less useful for risk assessment purposes, and care should be taken when averaging the results along with results from the other forms of sampling. Random sampling involves selecting monitoring locations in a random and unbiased manner, with no correlation between locations (other than, perhaps, the fact that they are all in a defined region). Assessors could establish locations by creating a grid, and then randomly selecting the two coordinates (x and y) in that grid. Random sampling has the advantage of well established and relatively easy to apply statistical methods for evaluating results, but runs the risk of missing some "hot spots" of exposure. Systematic sampling involves establishing a grid and placing monitors systematically on the grid nodes. This ensures that sampling is uniform across an area, although statistical analysis is more complex because the samples are not truly random. Exhibit 10-6 illustrates common types of sampling programs.

A typical monitoring station, located at a site with easy access, power, and protection for the equipment

There also are practical considerations in selecting locations, regardless of which of the three procedures above is used. Monitors and samplers will require access to land, both in terms of

permission to locate the equipment and the ability to reach the site. It must also be possible to provide electrical power, and some protection of the equipment against theft, vandalism, and other disturbance; therefore, a fence may be needed.

Exhibit 10-6. Common Types of Sampling



Purposive sampling focuses the sampling effort in specific locations (in this example, the area estimated to have the highest concentration). Most air quality sampling is purposeful (i.e., monitoring stations are located in areas where monitoring is feasible (e.g., locations that are accessible), areas of direct (e.g., maximum) impact, or where concerns about potential exposures have been raised). Grid sampling consists of regularly-spaced samples in a predetermined grid. Random sampling consists of samples in locations selected by chance.

- **Determining the types of equipment and samples**. The sampling/monitoring method will depend on the compound being sampled, as well as the need for grab samples or composite (continuous) monitoring. See Section 10.6.1 for more detail on this issue.

- **Conducting field screening**. Before establishing the monitoring site, it is useful to conduct some limited screening of the region using relatively simply methods. This will help identify locations likely to be of interest (e.g., likely locations of maximal exposure). If this isn't possible, modeling results might be used. Guidance on this issue can be found in EPA's *Field Screening Methods Catalog*.[8] These results generally should not, however, be used in

the risk assessment of chronic exposures because a small number of samples taken over a short period of time will not provide an accurate estimate of long term exposure.

- **Accounting for temporal and meteorological factors**. Sampling must account for the fact that concentrations will fluctuate in time, in part because of meteorology (e.g., the wind blows in different directions during the day, carrying the contaminant to different locations). Where variability is high, a larger number of samples will be needed to achieve a desired level of accuracy. The sampling program should include a full annual cycle covering the seasons for a chronic exposure assessment. Where this is not possible due to limits on resources, the sampling should at least include two temporal extremes (e.g., under windy conditions blowing from major sources to the monitor, and under calm conditions). It is essential to include the variability of the samples in any estimates of accuracy for the monitoring location.

- **Implementing QA/QC measures**. It is essential that well-established, clear and documented methods for assuring the quality and reliability of data be developed. Many of these issues are described in the text box on the QAPP discussed in Section 10.3. A **sampling protocol** must be developed detailing (1) conditions under which samples are collected; (2) how training of individuals will be conducted; (3) how the precision and accuracy will be ensured so results are obtained reproducibly; and (4) the analytical strategies that will be used to ensure quantitation limits are met. Measures are also put into place to ensure that samples are handled appropriately from collection through analysis (e.g., chain-of-custody requirements, allowable sample holding times).

  Field Blanks

  A field blank is a clean sample, carried to the sampling site, exposed to sampling conditions, returned to the laboratory, and treated as an environmental sample. Field blanks are used to demonstrate that:
  - Equipment cleaning has adequately removed contamination introduced by sampling at previous sites;
  - Sampling and sample processing have not resulted in contamination; and
  - Sample handling and transport, lab transport, and lab measurement have not introduced contamination.

  Sampling devices used to collect, store, preserve, and transport samples must not alter the sample in any way that complicates analysis. Samples should be stored in a way that keeps the concentration as close as possible to that in the field. QC samples must be collected, stored, transported, and analyzed in a way that is identical to the treatment of site samples. For example, both field and trip blanks, which are sampling devices that have not been used for sampling in the field but otherwise are brought through all of the other procedures to which field samples will be subjected, must be treated identically to the actual field samples. These field and trip blanks provide information on the extent to which samples might become contaminated by non-site-related materials during handling in the field (field blanks) and subsequent transport back to the lab for analysis (trip blanks).

10.5.2 Data Analysis and Reporting

As Section 10.4.1 mentions, adequate data analysis, recording, and archiving is essential to the design and conduct of a monitoring program. It is important that assessors enter each data point

into a file with relevant qualifiers, including location of sample; date and time of sample; method of sampling and relevant operating characteristics (e.g., flow rate); transfer process; storage time; analysis method; and identity of people performing all stages of the measurement. The integrity of this database should then be assessed periodically by comparing a random sample of file information against hard copies (e.g., laboratory books) to ensure reliability of transcription. For results using a common methodology, there should be a record of several key aspects of the method that assure reliability:

- A description of the calibration process, including certification of any standards used in that calibration.

- Results of any inter-laboratory comparison of uses of the method, and certification that the laboratory performing the analysis for the sampling program falls within a reasonable range of these inter-laboratory results.

- A record of background levels and levels in blanks, allowing a comparison of these against sample results.

- A summary of the frequency of "detects," or fraction of samples with values above the MDL or SQL (see Exhibit 10-7). If this fraction is small and the chemical is thought to be present, it may indicate that improvements in the method are needed. Of course, if the SQLs are well below any health benchmark, a small fraction of detects or quantifiable results need not trigger a call for improvements.

- A policy on significant digits and how these are related to the accuracy of the method. All results should be reported only with a number of digits consistent with this accuracy. In addition, rounding rules should also be established and followed.

- A description of how summary quantities such as means are calculated. This description includes such factors as how outliers are identified and dealt with, the possible influence of this process on sample mean and variance, and how results below the SQL are handled. For example, some laboratories will report a chemical that they detect below the SQL as "not detected" simply because it is below the SQL and they cannot accurately quantify it. Other labs will report such a chemical as detected, but with an estimated concentration and qualify the value as "J." In general, labs should report detected chemicals, regardless of whether they can accurately quantify their concentration. The use of J-qualified data for risk assessment purposes is described below.

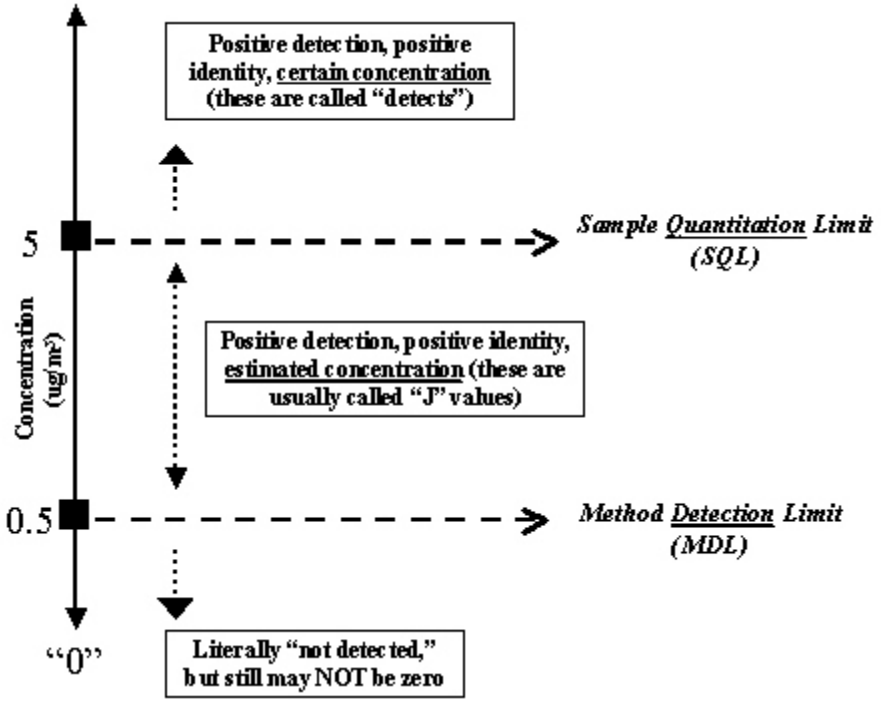
- A detailed description of the QA/QC flags that are used by the lab to report data and a clear description of how the lab deals with samples that are associated with blanks that are contaminated.

10.5.3 The Use of Monitoring Data to Calculate Exposure Concentrations

As the above noted, monitoring data can, under limited circumstances, be used to estimate exposure concentrations in the vicinity of the monitor. Some general rules that apply to this activity are as follows:

- Data from different monitors should not be combined to estimate exposure concentrations (with the exception of co-located duplicate monitors – see below).

Exhibit 10-7. Illustration of SQL and MDL



People often refer to the SQL as the "detection limit." When a lab reports a result as "undetected" (U) or "not detected" (ND), this is the level to which they are usually referring. The SQL is really a limit of quantitationthat can vary between samples (the MDL, on the other hand, is a true "detection limit"). For example, a result of "5U μg/m3" usually means "not detected at a sample-specific quantitation limit of 5 μg/m3." When a chemical is detected, but below the SQL (i.e., a "J" value), risk assessors often use the J value as is (i.e., the J value is used with no modification). When a chemical is not detected in a sample, but there is reason to believe it may be present, even at very small amounts (e.g., the chemical is found in some samples, but not in others), risk assessors often use ½ the SQL as a surrogate concentration for risk assessment purposes (in the example above, half of "5U" is 5/2 = 2.5). It is usually not appropriate to use ½ the MDL as a surrogate for concentration for exposure assessment purposes. The process of assessing and combining monitoring data for exposure assessment purposes is discussed in more detail in Appendices H and I.

- Monitoring data at a location are not generally used to describe variation of exposure concentrations experienced by individuals in a population of people, although temporal differences for the population as a whole (e.g., exposure to the population during the winter versus exposure to the population during the spring) may be appropriate. Variation in exposure concentration within a population is preferably described by looking at exposure concentrations across a set of monitors in the assessment area.

- The representativeness of the exposure concentrations, as represented by any one monitor's data, depends on the amount and quality of the data collected, and the individual chemicals involved. For example, some pollutants may be "regional" in nature, meaning that their concentration tends to be relatively homogeneous over a large area. In that case, a given monitor may be broadly representative of ambient concentrations throughout the region. Some compounds, on the other hand, show sharp

concentration gradients over space and the monitor may only be reflective of exposure concentrations for people living very near to the monitoring station.

- To assess acute exposures with monitoring samples, the results from the individual samples (not their average) should be compared to acute health benchmarks, and the sampling time should match the averaging time of the acute health benchmark (see Chapter 13).

- For chronic exposure assessment, all the valid samples collected and analyzed for a monitor (taken routinely throughout the course of at least one year) are averaged (see below) to provide an estimate of the long term exposure concentration.

Appendix I provides a general overview of how monitoring data should be evaluated, processed, and displayed to develop estimates of exposure concentration.

10.6 Monitoring Methods, Technologies, and Costs

EPA has developed a number of methods to measure the concentration of air toxics in ambient air. The majority of this information is found on EPA's Ambient Monitoring Technology Information Center (AMTIC) website (Exhibit 10-8), and assessors involved in monitoring should become familiar with this website and its contents. Given the breadth and scope of this website's contents, it is not possible here to fully review all of the information here. This section only provides an introduction to the methods. Appendix E summarizes relevant information from two key EPA compendia of methods, primarily for ambient air monitoring. In addition, this chapter does not examine indoor air measurements, as EPA has provided monitoring recommendations only for radon.

EPA has developed a *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* to assist federal, state, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air (Exhibit 10-9).[9] The Compendium contains a set of 17 peer-reviewed, standardized methods for the determination of volatile, semi-volatile, and selected toxic organic pollutants in the air. The Compendium, along with updates and addenda, is available at EPA's AMTIC Website at http://www.epa.gov/ttn/amtic/airtox.html.

Exhibit 10-8. EPA's Ambient Monitoring Technology Information Center (AMTIC)

Information on ambient concentrations for a wide variety of compounds can be found through AMTIC (http://www.epa.gov/ttn/amtic/welcome.html). This Center facilitates the exchange of ambient monitoring-related information collected throughout the U.S., and can provide valuable insights into the selection of monitoring methods. Established in 1991 as an electronic bulletin board system (BBS), AMTIC has evolved with changing technology into a page on the World Wide Web. It is operated by EPA's OAQPS through the Monitoring and Quality Assurance Group (MQAG). The database contains information on all the Reference and Equivalent Methods for the criteria pollutants, the toxic organic (TO) Methods for air toxics and other noncriteria pollutant methodologies, Federal Regulations pertaining to ambient monitoring, ambient monitoring QA/QC related information, information on ambient monitoring related publications, ambient monitoring news, field and laboratory studies of interest, and updates on any new or developing EPA Ambient Air standards.

Exhibit 10-9. EPA's Toxic Organic (TO) Monitoring Methods	
Method	**Description**
TO-1	Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)
TO-2	Method for the Determination of VOCs in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)
TO-3	Method for the Determination of VOCs in Ambient Air using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection
TO-4A	Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)
TO-5	Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)
TO-6	Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography (HPLC)
TO-7	Method for the Determination of nitrosodimethylamine (NDMA) in Ambient Air Using Gas Chromatography
TO-8	Method for the Determination of Phenol and Methylphenols (Cresols) in Ambient Air Using High Performance Liquid Chromatography
TO-9A	Determination of Polychlorinated, Polybrominated, and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air
TO-10A	Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)
TO-11A	Determination of Formaldehyde in Ambient Air using Adsorbant Cartridge Followed by High Performance Liquid Chromatography (HPLC)
TO-12	Method for the Determination of Non-methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)
TO-13A	Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)
TO-14A	Determination of VOCs in Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography
TO-15	Determination of VOCs in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)
TO-16	Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases
TO-17	Determination of VOCs in Air Using Active Sampling Onto Sorbent Tubes

10.6.1 Ambient Air Monitoring Methods and Technologies

The term "monitoring method" is a comprehensive term that includes everything from the sample collection devices to analytical laboratory methods. These methods fall into three broad categories related to the **time scale over which concentration will be averaged**:

- **Grab samples** provide a quasi-instantaneous measurement of a concentration. They generally are obtained in the field usually over a period of 24 hours or less and then returned to the laboratory for analysis. The sampling may be automated, allowing a time-series of samples to be drawn, but all samples still are generally returned to the laboratory for analysis. In rare instances, a mobile laboratory may be co-located with the sampling location, in which more "real-time" data is possible.

- **Continuous monitors** provide a time series of measurements in the field, with a stream of data at selected intervals (e.g., once each 24 hours). These monitors may be fully automated versions of grab sampling, taking samples at a set interval but then analyzing the samples internally rather than returning to the lab. An alternative is a continuous flow monitors, which draw ambient air through a chamber and analyzes it in real time (e.g., the semi-continuous formaldehyde monitor developed by the EPA, which runs through one complete cycle of sampling and analysis in 10 minutes).

- **Time-integrated samples** are collected over an extended period of time. Only the total pollutant collected is measured, and so only the average concentration during the sampling period can be determined. As with grab samples, these measurements generally are obtained in the field and returned to a laboratory for analysis.

Monitoring methods/systems can also be divided into a different set of categories based on the **method of collection**:

- **Integrated air sampling devices** use a pump to draw air continuously into the sample chamber, over a reactive medium, or through a filter during a prescribed period of time; the sample is returned to the laboratory for analysis.

- **Direct-read monitors** draw air through a measurement system and provide a direct reading of the concentration without returning samples to the lab.

- **Automated monitoring systems** collect samples, perform the analysis, and report results at regular intervals in the field.

- **Air deposition monitors** rely on deposition properties of compounds (e.g., particulates), and may consist of active and/or passive, wet and/or dry sampling methods.

- **Passive monitors** allow the compound to diffuse into contact with an active material; these generally are analyzed in the lab, although some indicate the presence of a compound by a color change.

- **Grab sampling devices** use an essentially instantaneous sampling method, such as an evacuated chamber into which ambient air is allowed to enter at a fixed rate; the sample collected is returned to the laboratory for analysis.

In some circumstances, grab samples may be collected by volunteers (for example, when residents near an industrial complex organize to capture samples when a strong odor is present). This process is commonly referred to as a "bucket brigade." Bucket brigades may provide useful information that a problem may exist that warrants more in-depth evaluation. They are also helpful, in some circumstances, to help the affected community become more involved in the air toxics evaluation process. Nevertheless, care should be taken to ensure that all of the necessary sampling and analysis protocols and QA/QC are established, understood, and followed by the bucket brigade team members to ensure that the grab samples are of sufficient quality to be used for decision making purpose at hand.

Mobile air monitoring platforms are sometimes used to evaluate air quality parameters. A "mobile platform" can be anything from a VOC sampling apparatus on a movable trailer to a sophisticated multi-pollutant sampling and analytical mobile trailer. The utility of mobile platforms is that they can be moved from place to place relatively easily (e.g., for hotspots analysis) and may only require a place to park the platform and an electrical hookup (as opposed to the more difficult process of establishing fixed monitoring locations, which requires access to land, often by establishing a leasing agreement, and permanent security measures, such as fencing).

Most existing air toxics monitoring programs have focused on the 188 HAPs, and especially on the 33 urban HAPs identified by OAQPS on a nationwide basis (Exhibit 10-10) as generally presenting the greatest contribution to risk to public health from air toxics in urban areas. Note that the highest-risk HAPs in a specific region or community may differ from this list. A significant database exists on national exposures to these compounds, especially those monitored by the National-Scale Air Toxics Assessment (see Chapter 2 and the website at www.epa.gov/ttn/atw/nata). A general starting point for most monitoring efforts should be an initial screening analysis to identify the COPCs. A description of the general process for screening analyses of this type is provided in Chapter 1.

Exhibit 10-10. 33 Urban HAPs (Nationwide Basis)

acetaldehyde	f*ormaldehyde*
acrolein	hexachlorbenzene
acrylonitrile	hydrazine
arsenic and compounds	*lead and compounds*
benzene	*manganese and compounds*
beryllium and compounds	mercury and compounds
1,3-butadiene	*methylene chloride*
cadmium and compounds	*nickel and compounds*
carbon tetrachloride	polychlorinated biphenyls
chloroform	polycylic organic matter
chromium and compounds	propylene dichloride
coke over emissions	quinolene
1,2-dichloropropane	1,1,2,2-tetrachloroethane
dioxin	*tetrachloroethylene*
ethylene dibromide	*trichloroethylene*
ethylene dichloride	*vinyl chloride*
ethylene oxide	

Compounds monitored in the NATA National Scale Assessment pilot sites are indicated by *italics*.

EPA has not developed methods for many compounds, including some of the 33 urban HAPs. Potential deficiencies in particular monitoring methods include:

- Quantitation limits are not low enough relative to environmental levels and/or health benchmarks;
- Lack of available standards for monitoring protocols (e.g., standards developed by the National Institute of Science and Technology);
- Methods are not practical or easy to implement;
- Compound stability is so poor that the compound degrades significantly between the time it is collected and the time it is analyzed, resulting in poor to no recovery at the time of analysis;
- Recover efficiencies are too low, resulting in poor precision and/or quantitation limits that are not low enough for use relative to health benchmarks;
- Methods have not been sufficiently tested in the laboratory and field;
- Methods are not producing results that are comparable to established methods; and
- Poor reliability.

The deficiencies noted in Exhibit 10-11 are particularly important and have been identified by EPA as needing methodology development.[10] Because they present a similar challenge, EPA has targeted several VOCs for programs to improve monitoring capabilities (Exhibit 10-12). In addition, both diesel exhaust (a complex mixture), acrolein, and arsenic require additional method development to yield accurate, reliable, and field-tested monitoring methods.

10.6.2 Sampling Costs

There is no general guideline for the costs associated with monitoring programs, as they depend on quite an array of factors. Several of the more critical include:

- Whether samples are analyzed "in house" or contracted out.
- Whether monitoring equipment is available or must be purchased or leased.
- The number of monitoring results or samples required (there is some economy of scale, but increased numbers of results also increases cost).
- Whether personnel must be hired and/or trained.
- The potential cost of leases and insurance for monitoring sites.
- Laboratory analytical costs for special analytes. For example, dioxin samples can run as high as $1,000 per sample, making an extensive dioxin sampling scheme generally out of reach for most studies.

10.7 Archiving Air Toxics Monitoring Data

When appropriate, results of a monitoring program should be submitted to the relevant air toxics database, such as EPA's Air Quality System (AQS).[11] The AQS website (www.epa.gov/ttn/airs/airsaqs/sysoverview.htm) provides detailed information on submitting and retrieving such data, including instructions on the file format for the data. Archived data may be accessed at the AQS site.[12]

Exhibit 10-11. Identified Deficiencies in Available Monitoring Methods		
Compound	**Candidate Method**	**Deficiency**
1,3-butadiene 1,2-dibromoethane 1,2-dichloroethane	TO14A/15	sensitivity issue; false highs
acrylonitrile	TO14A/15	NIST standard needed; recovery problems
ethylene oxide	None/NIOSH 1614	poor storage stability
1,1,2,2-tetrachloroethane	TO-15	NIST standard needed
arsenic and compounds	IO-3	sensitivity issues; filter contamination; resource intensive
beryllium and compounds	None	resource intensive; XRF sensitivity issue
mercury and compounds	IO-5	requires special equipment
acrolein	None	TO-11A results in unstable derivative poor recovery
2,3,7,8-tetrachlorodibenzo-p-dioxin	TO-9A	resource intensive

Exhibit 10-12. VOC Compounds Needing Improved Monitoring Methods	
vinyl chloride	cis- and trans-1,3-dichloropropene
1,2-dichloroethene	1,1,2-dichoroethane
dichloromethane	1,2-dibromoethane
chloroform	tetrachloroethylene
1,2-dichloroethane	1,1,2,2-tetrachloroethane
benzene	hexachlorobutadiene
carbon tetrachloride	acrylonitrile
1,2-dichloropropane	1,3-butadiene
trichloroethene	ethylene oxide

10.8 Using Air Monitoring Data to Evaluate Source Contribution

Caution should be used in interpreting the results of a measurement as being uniquely associated with a given source. Most measurements from monitoring data are, depending on the chemical, a combination of background concentrations and the same chemical released from possibly multiple sources. Benzene, for example, is present in background air, is released from mobile sources, and is used and released from multiple types of stationary sources. This is not to say that monitoring data cannot be used to identify releases from a source. Under certain circumstances, analysis of multiple measurements at different locations may indicate a spatial pattern consistent with the known air dispersion pattern accompanying that source (and inconsistent with the patterns from other sources).

Use of Historical Monitoring Data

Historical monitoring data for an assessment area may be of use in developing the analysis plan. They can help with a range of uses, including:

- Identifying the types of chemicals that may be present in the air;
- Selecting locations for monitors;
- Performing preliminary screening level risk estimates; and
- Establishing acceptable monitoring protocols.

The utility of historical data will, of course, be based on an assessment of the quality of the data. For example, data that were not collected with sufficient QA/QC, may not be useful for any of the above purposes.

EPA also has developed "receptor models" which make use of monitoring data, together with emissions inventories, to perform source apportionment analyses, which provide a quantitative estimate of what percent of each pollutant comes from each identified source. EPA's Chemical Mass Balance Model is one such example (available on EPA's SCRAM website at http://www.epa.gov/scram001/tt23.htm). This model uses chemical concentrations measured in samples from sources (emissions) and receptor locations to estimate the contributions of source types to ambient air pollutant concentrations. The model is used primarily in the development of State Implementation Plans for PM_{10}. The model allows the user to select samples, chemical species, and source types for modeling, calculate source contributions and their standard errors, evaluate goodness-of-fit and validate the model results, prepare output documentation, and graph results.

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